

Bis[1-(4-chlorobenzyl)-3-methylpyrazinium] bis(maleonitriledithiolato)nickelate(II)

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$

R factor = 0.032

wR factor = 0.082

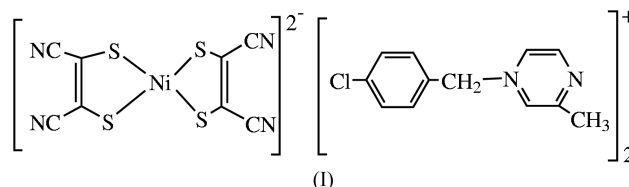
Data-to-parameter ratio = 14.0

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The synthesis and crystal structure of the novel ion-pair title complex, $(\text{C}_{12}\text{H}_{12}\text{ClN}_2)_2[\text{Ni}(\text{C}_4\text{N}_2\text{S}_2)_2]$ or $[\text{ClBzMePz}]_2[\text{Ni}(\text{mnt})_2]$ [where ClBzMePz is 1-(4-chlorobenzyl)-3-methylpyrazinium and mnt is maleonitriledithiolate], is reported. The structural study shows that the asymmetric unit consists of one cation and one-half of an anion; the Ni atom lies at a centre of symmetry. The $[\text{ClBzMePz}]^+$ ion adopts an essentially planar conformation where both the phenyl ring and the pyrazine ring are twisted with respect to the plane of the C—N—C chain which links them. It is worth noting that the anions and cations of the title complex stack in well-separated columns, and the intermolecular contacts between anions and cations observed in the crystal structure may play an important role in the crystal packing.

Comment

Maleonitriledithiolate (mnt^{2-}) transition metal complexes have attracted wide interest, mainly due to their versatile structural, chemical and physical properties, such as electrical conductivity, photoconductivity and magnetic coupling (Robertson & Cronin, 2002; Canadell, 1999). The discovery in 1996 of the ferromagnetic complex containing the $\text{Ni}(\text{mnt})_2^{2-}$ ion, $\text{NH}_4[\text{Ni}(\text{mnt})_2]\cdot\text{H}_2\text{O}$, greatly stimulated interest in $\text{Ni}(\text{mnt})_2$ complexes as building blocks for new molecular magnets (Coomber *et al.*, 1996). Recently, ion-pair complexes containing the $\text{Ni}(\text{mnt})_2^{2-}$ ion have been intensively studied (Urichi *et al.*, 1998; Ren *et al.*, 2002; Pullen *et al.*, 1998; Xie *et al.*, 2002) and the topology and size of the counter-ions of the $\text{Ni}(\text{mnt})_2^{2-}$ ion play an important role in tuning the stacks of anions and cations. We report here the synthesis and crystal structure of the ion-pair complex $[\text{ClBzMePz}]_2[\text{Ni}(\text{mnt})_2]$ [where ClBzMePz is 1-(4-chlorobenzyl)-3-methylpyrazinium], (I). To the best of our knowledge, ion-pair $\text{Ni}(\text{mnt})_2^{2-}$ complexes containing substituted pyrazinium cations are very rare.



The molecular structure of (I) is shown in Fig. 1. There are two $[\text{ClBzMePz}]^+$ cations and an $\text{Ni}(\text{mnt})_2^{2-}$ anion. For the $\text{Ni}(\text{mnt})_2^{2-}$ anion, four S atoms define a plane and the Ni atom exhibits square-planar coordination geometry. The five-membered nickel-containing rings are slightly puckered. The

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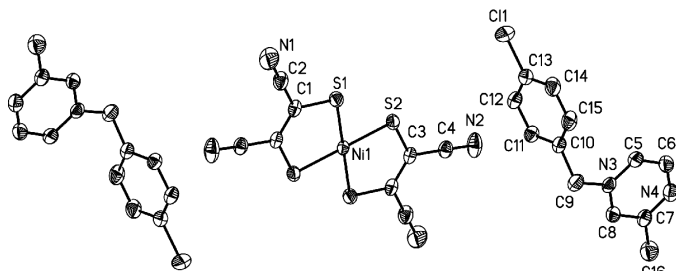


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 30% probability level. All H atoms have been omitted for clarity.

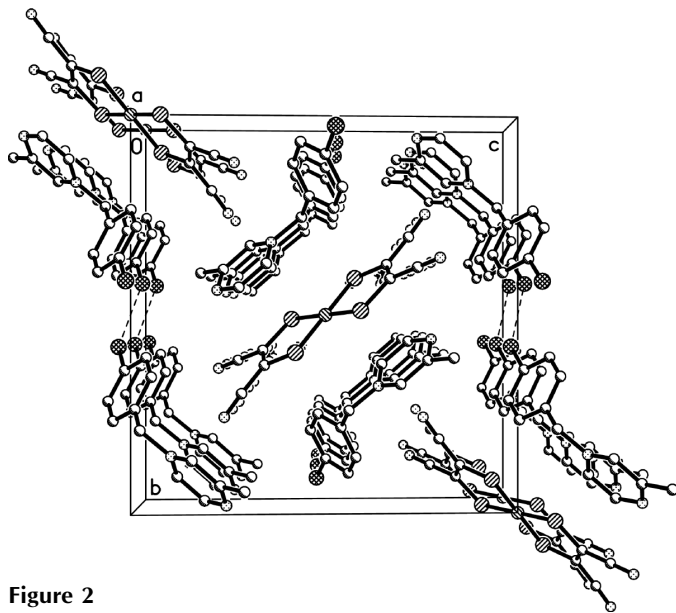


Figure 2
The crystal packing of the title complex, viewed down the *a* axis.

Ni—S bond distances are 2.1648 (6) and 2.1662 (7) Å and the S—Ni—S chelate bite angle is 92.80 (3)°; these values compare well with those found in other Ni(mnt)₂²⁻ complexes (Bulgarevich *et al.*, 1994). The CN groups are slightly tilted out of the plane; the deviations from the plane are 0.234 (6) Å for N1 and −0.478 (6) Å for N2. The [CIBzMePz]⁺ ion adopts a conformation where the benzene and pyrazine rings are twisted with respect to the C10/C9/N3 reference plane. The benzene and pyrazine rings are both planar. The deviation of the Cl atom from the benzene ring is 0.010 (8) Å and the deviation of atom C16 from the pyrazine ring is 0.026 (1) Å. The dihedral angles which the pyrazine and benzene rings make with the C10/C9/N3 reference plane are 138.8 (2) and 90.8 (2)°, respectively. The benzene and pyrazine rings have a dihedral angle of 109.4 (2)° between them. The S1/S2/Ni1/S1ⁱ/S2ⁱ [symmetry code: (i) (i) $-x, 2 - y, -z$] plane makes dihedral angles of 104.0 (2) and 5.9 (2)° with the benzene and pyrazine rings, respectively.

The Ni(mnt)₂²⁻ anions and [CIBzMePz]⁺ cation form well-separated columns along the *a* axis of the crystallographic unit cell (Fig. 2). The closest Ni···Ni separation within a column of anions is 6.94 (2) Å and the closest Ni···Ni separation between columns of anions is 11.53 (2) Å. Three anion–cation intermolecular interactions are observed in the crystal structure: C9—H9···S2ⁱⁱ, with a C9···S2ⁱⁱ distance of 3.684 (3) Å;

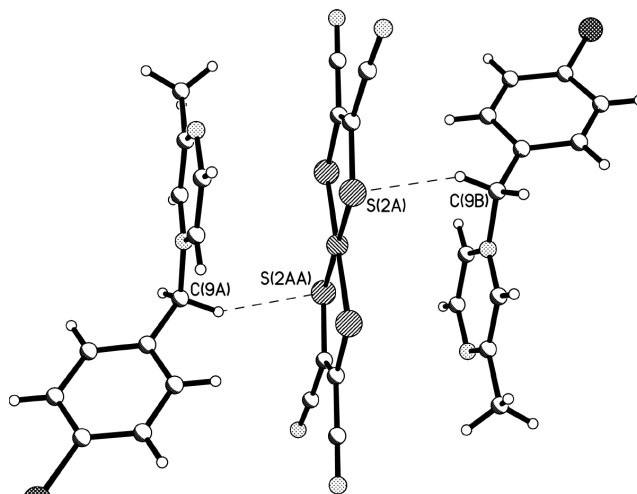


Figure 3
One of the interactions between the cations and anions.

C11—H11···N1ⁱⁱⁱ, with a C11···N1ⁱⁱⁱ distance of 3.407 (4) Å; and a π – π interaction between Ni1/S1/C1/C1ⁱ/S1ⁱ and the benzene ring, with a distance of 3.60 (2) Å [symmetry codes: (ii) $-x, 1 - y, 1 - z$; (iii) $x - \frac{1}{2}, \frac{3}{2} - y, \frac{1}{2} + z$]. These anion–cation contacts may play an important role in the crystal packing.

Experimental

1-(4-Chlorobenzyl)-3-methylpyrazinium bromide ([CIBzMePz]Br) and disodium maleonitriledithiolate (Na₂mnt) were synthesized following published procedures (Davison & Holm, 1967; Kobayashi & Sasaki, 1977). [CIBzMePz]₂[Ni(mnt)₂] was prepared by the direct combination of 1:2:2 molar equivalents of NiCl₂·6H₂O, Na₂mnt and [CIBzMePz]Br in H₂O. The resulting red precipitate was filtered off, washed with water and dried under vacuum (yield: 86%). Red single crystals of (I) suitable for X-ray analysis were grown from CH₃CN by slow evaporation of the solvent at room temperature over a period of about a week. Analysis calculated for C₃₂H₂₄Cl₂N₈NiS₄ (%): C 49.38, H 3.10, N 14.39; found: C 49.32, H 3.19, N 14.29. IR data (cm⁻¹): 3003 (*w*), 2934 (*w*), 2218 (*m*), 2199 (*s*), 1613 (*m*), 1597 (*m*), 1561 (*m*), 1546 (*m*), 1492 (*s*), 1478 (*s*), 1411 (*m*), 1286 (*m*), 1151 (*s*), 1086 (*s*), 859 (*s*), 824 (*s*), 810 (*s*), 770 (*s*), 709 (*m*), 670 (*m*), 609 (*m*), 554 (*w*), 508 (*s*), 487 (*m*), 421 (*m*).

Crystal data

(C₁₂H₁₂ClN₂)₂[Ni(C₄N₂S₂)₂]
M_r = 778.44
 Monoclinic, *P*₂₁/*n*
a = 6.940 (2) Å
b = 15.994 (4) Å
c = 15.573 (4) Å
 β = 93.93 (1)°
V = 1724.5 (8) Å³
Z = 2

D_x = 1.499 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 918 reflections
 θ = 2.6–25.8°
 μ = 1.00 mm⁻¹
T = 293 (2) K
 Block, red
 0.3 × 0.2 × 0.2 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2000)
T_{min} = 0.79, *T_{max}* = 0.82
 8430 measured reflections

3014 independent reflections
 2467 reflections with *I* > 2 σ (*I*)
R_{int} = 0.040
 θ_{max} = 25.0°
h = −8 → 8
k = −18 → 19
l = −14 → 18

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.082$
 $S = 1.08$
 3014 reflections
 215 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.04P)^2P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.37 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$

All H atoms were positioned geometrically (C–H = 0.93–0.97 Å) and refined as riding, with $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{parent atom})$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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References

- Bruker (2000). *SMART, SAINT, SADABS and SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bulgarevich, S. B., Bren, D. V., Movshovic, D. Y., Finocchiaro, P. & Failla, S. (1994). *J. Mol. Struct.* **317**, 147–152.
- Canadell, E. (1999). *Coord. Chem. Rev.* **185–186**, 629–651.
- Coomber, A. T., Beljonne, D., Friend, R. H., Bredas, J. L., Charlton, A., Robertson, N., Underhill, A. E., Kurmoo, M. & Day, P. (1996). *Nature (London)*, **380**, 144–146.
- Davison, A. & Holm, R. H. (1967). *Inorg. Synth.* **10**, 8–12.
- Kobayashi, A. & Sasaki, Y. (1977). *Bull. Chem. Soc. Jpn.* **10**, 2650–2653.
- Pullen, A. E., Faulmann, C., Pokhodnya, K. I., Cassoux, P. & Tokumoto, M. (1998). *Inorg. Chem.* **37**, 6174–6720.
- Ren, X. M., Meng, Q. J., Song, Y., Lu, C. L., Hu, C. J., Chen, X. Y. & Xue, Z. L. (2002). *Inorg. Chem.* **41**, 5931–5933.
- Robertson, N. & Cronin, L. (2002). *Coord. Chem. Rev.* **227**, 93–127.
- Urichi, M., Yakushi, K., Yamashita, Y. & Qin, J. (1998). *J. Mater. Chem.* **8**, 141–146.
- Xie, J. L., Ren, X. M., Song, Y., Zhang, W. W., Liu, W. L., He, C. & Meng, Q. J. (2002). *Chem. Commun.* pp. 2346–2347.